Plasma-catalytic Removal of Formaldehyde in Atmospheric Pressure Gas Streams

DING Huixian, ZHANG Zengfeng
(Heilongjiang Institute of Science & Technology, Harbin 150027, PR China
E-mail: huixianding@yahoo.cn. E-mail: zzf64@163.com)

Abstract: Formaldehyde is a major indoor air pollutant and it is able to cause serious health disorders in residents. Major conventional techniques in removing formaldehyde from gas streams include absorption, adsorption, catalytic and photo-catalytic oxidation processes. Low efficiency, high energy consumption and harmful byproducts are major problems in these methods. This work combined dielectric barrier discharge (DBD) plasmas with Ag/CeO_2 catalysts, and achieved lower energy consumption (-90 eV/molecule of HCHO), higher GHVS (16500 h^{-1}), high oxidative conversion into CO_2 (86%) and high removal efficiency (99%) to remove formaldehyde in gas streams at atmospheric pressure, when a feed gas mixture of 276 ppm HCHO, 21.0% O_2, 1.0% H_2O in N_2 was used. Experimental results indicate that the plasma-generated short-lived gas phase radicals, such as O, OH and HO_2, play important roles in the catalytic redox circles of Ag/CeO_2 to oxidize HCHO and CO to CO_2.

Keywords: Formaldehyde, plasma, Catalysis

1 INTRODUCTION

Formaldehyde (HCHO) is one of the most common volatile organic compounds (VOCs), which is able to cause health disorders in residents, including irritation of the eyes and respiratory tract, nausea, headache, fatigue, dullness and thirst (US EPA, 1991). The major emission sources of formaldehyde include production facilities of urea-formaldehyde, phenol-formaldehyde resins and some buildings materials, such as plywood, chipboard and paneling. Formaldehyde is also a primary indoor air pollutant emitted mainly from the above building materials. In our previous paper [1], the removal of formaldehyde from gas streams via alumina-pellet-filled dielectric barrier discharge (DBD) plasmas at atmospheric pressure and 70 ℃ was reported. The preceding investigations regarding different formaldehyde removal techniques, especially its plasma-induced destruction studies, were summarized in Ref. [1]. Only a brief description of the plasma-involved work is outlined here. Storch and Kushner [2] conducted a theoretical modeling concerning HCHO destruction from $N_2/O_2/H_2O$/HCHO gas streams by using low temperature plasmas and concluded that the destruction of HCHO mainly resulted from the chemical attacks by plasma-generated OH and O radicals. Chang and Lee [3] reported the first experimental study on HCHO gas-phase removal in a DBD reactor at room temperature. At GHSV of ~250 – 500 h^{-1} (GHSV = gas flow volume per hour/discharge volume), about 97% – 90% of HCHO (100 ppm in air) was destructed. Recently, Hensel et al. [4] studied the effects of discharge mode, discharge polarity and other experimental factors onto the formaldehyde removal in streamer corona discharges. With 190 ppm HCHO in air, a moderate GHSV of -1000 h^{-1} and input discharge energy density, E_{in}, of -200 J l^{-1}, about 60% of HCHO can be converted.

One obvious problem of the pure plasma-induced removal processes for VOCs' was the high yield of byproducts. In our previous work reported by us in Ref. [1], the ratio of CO and CO_2 produced via barrier discharges over γ-Al_2O_3 pellets was as high as about 1 to 1. In the last decade, it has been found in some cases that the problems can be partially solved by the synergistic effects of non-thermal plasmas and appropriate catalysts ([5-8] and the references cited therein).

The present work reports investigations on HCHO oxidative removal by using a DBD tube reactor filled with Ag/CeO_2 catalyst pellets in the discharge zone. In comparison with the γ-Al_2O_3 pellet filled DBD plasmas [1], the significantly higher HCHO removal efficiency and much higher CO_2 selectivity in the product gas have been obtained. The possible mechanisms to generate the synergistic effects between the plasma and catalyst in HCHO and CO oxidation processes, as well as the HCHO specific energy consumption per HCHO molecule converted will be discussed.

2 EXPERIMENTAL

Ag/CeO_2 catalyst with 7 (wt) % Ag was prepared by an impregnation method. Typically, the impregnated mixture, formed by dispersing CeO_2 powders into 1.2 M $AgNO_3$ aqueous solution, was dried at 110 ℃ for 12 h and calcinated at 500 ℃ for 6 h in an Ar flow. The CeO_2 powders used in the above procedure were prepared by a homogenous precipitation method. Initially, the mixed 0.3 M $(NH_2)_2CO$ (urea) and 0.05 M $Ce(NO_3)_3$ aqueous solutions were stirred at 80 ℃ for 10 h. Then, the appeared white precipitate with the original solution was aged for 12 h at 80 ℃ without stirring. After filtering and washing, the precipitate was dried at 110 ℃ for 12 h and calcinated at 500 ℃ for 5 h in air.

The specific surface areas of thus prepared Ag/CeO_2 catalyst used in the experiment , were measured to be -88 $m^2 g^{-1}$.

The whole experimental setup used in this work for HCHO removal has been described in details in Ref. [1]. Only a brief summary is outlined here. The plasma-catalytic reactor used in this work consists of a fused silica tube (id 10 mm), a stainless steel rod (od 2 mm) placed along the axis of the outer tube as the high-voltage electrode and catalyst pellets (20-40 mesh, 2.2 ml in stack volume) filled between the outer tube and the rod. A stainless steel wire mesh (30 mm in length along the reactor axis) wound on the outside surface of the outer tube was used as the ground electrode. In order to reduce the time period to reach the adsorption equilibrium for HCHO on the catalyst pellets, a reaction temperature of 70 °C was always used in this work.

The DBD power supply source is capable of supplying a bipolar sine wave output with 0-40 kV peak-to-peak voltage (U_p) at an ac frequency of 50 Hz. The input electric discharge power at a certain experimental condition was measured via the area of the voltage-charge Lissajous figures [11]. The input discharge energy density, E_{in} in J l^{-1}, can be varied through adjusting U_p.

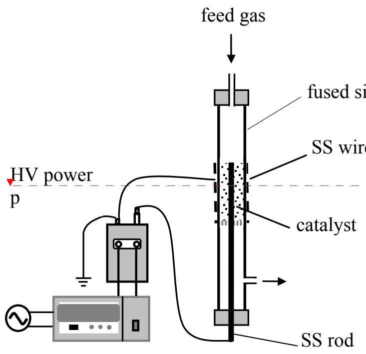

Fig. 1 The schematic of the plasma-catalytic reactor

Four mass-controlled gas flows (N_2, $HCHO/N_2$, H_2O/N_2, and O_2, see Fig. 1 of Ref. [1]) were premixed before entering the plasma-catalytic reactor. In order to examine the effects of H_2O and O_2 onto the HCHO removal, high purity (>99.99%) N_2 and O_2 gases were used. The formaldehyde gas was produced via catalytic depolymerization of trioxymethylene vapor in a N_2-diluted gas flow at 160 ℃ over glass pellets coated with phosphoric acid. The trioxymethylene vapor was generated by heating trioxymethylene solid at -40 ℃, controlled by a water bath, in a N_2 gas stream. The amount of H_2O in the feed gas can be controlled via adjusting the H_2O/N_2 flow rate as well as the temperature of the water bath. A typical feed gas mixture (276 ppm HCHO, 21.0% O_2, 1.0% H_2O in N_2) was used in majority of the experiments in this paper. In all the experiments, a feed gas flow rate of 605 ml/min, which corresponds to GHSV of 16500 h^{-1}, was always used. The HCHO concentration was analyzed by a gas chromatograph (SRI-8610C) with a 2m-long Porapak T column operating at 100 ℃. The concentrations of CO, CO_2 and N_2O in the outflow gas were determined by an infrared absorption spectrometer (SICK-MAIHAK-S710). NO and NO_2 concentrations in the outflow gas were monitored by a chemiluminescence analyzer (Monitor, ML9841AS).

3 RESULTS AND DISCUSSION

3.1 Synergistic Effects between the Plasma and Catalyst in HCHO and CO Oxidation

Fig. 2 shows the HCHO conversion percentage to CO_x (CO_x = CO+CO_2), $P(HCHO \rightarrow CO_x)$, and to CO_2, $P(HCHO \rightarrow CO_2)$, as functions of the input discharge energy density, E_{in}, via using the plasma-catalytic reactor filled with Ag/CeO_2 pellets or filled with fused silica pellets and the standard feed gas mixture (276 ppm HCHO, 21.0% O_2, 1.0% H_2O in N_2) with GHSV of 16500 h^{-1} (same GHSV was used in all of the experiments and it will not be mentioned in the following text). Over the whole E_{in} range investigated, both $P(HCHO \rightarrow CO_x)$ and $P(HCHO \rightarrow CO_2)$ show monotonic increase with the rising E_{in}. Dielectric barrier discharges usually consist of numerous random-distributed (both in the temporal and spatial domain) filament-like micro-discharge pulses [9]. At a certain electrode arrangement and a certain gas composition and pressure, the breakdown voltage U_{br} to form the micro-discharges is a constant. Since the applied voltage U_p is larger or much larger than U_{br}, the higher U_p is able to bring more breakdowns among one sine wave period. Therefore, larger E_{in}, obtained via raising U_p, can generate more electrons with sufficient energy and these electrons are able to produce more reactive intermediates and other subsequent reactions beneficial to the formaldehyde removal.

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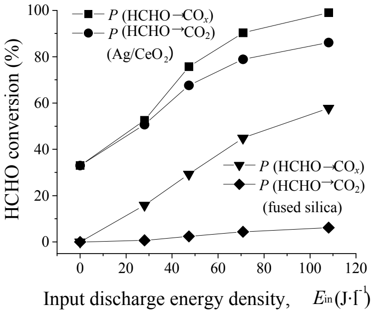

Fig. 2 Dependence of formaldehyde conversion percentages, $P(HCHO \rightarrow CO_x)$ and $P(HCHO \rightarrow CO_2)$, on input discharge energy density, E_{in} (276 ppm HCHO, 21.0% O_2, 1.0% H_2O in N_2)

At E_{in} = 108 J·l^{-1}, $P(HCHO \rightarrow CO_x)$ and $P(HCHO \rightarrow CO_x)$, which can be treated as a scale of the total HCHO removal efficiency, obtained from discharges over Ag/CeO_2 and fused silica pellets are 99% and 57%, respectively. Since the specific surface area of fused silica pellets is nearly zero, the quite large HCHO destruction percentage over them (57%) means that the pure plasma-induced destruction processes, i.e. the consecutive destructions of HCHO and HCO via collisions with plasma-generated radicals, O_2 and N_2 metastable species [1], play important roles in the total HCHO removal.

From the data shown in Fig. 2, the values of $P(HCHO \rightarrow CO_x)$ from pure plasma-induced (discharges over fused silica pellets, E_{in}=108 $J \cdot l^{-1}$), pure catalytic (over Ag/CeO_2 without discharges, E_{in} = 0 $J \cdot l^{-1}$) and plasma-catalytic oxidation (discharges over Ag/CeO_2, E_{in}=108 Jl^{-1}) of HCHO are 57%, 33% and 99%, respectively, and the values of $P(HCHO \rightarrow CO_2)$ on the conditions above are 6%, 33% and 86%, respectively. It is implied that there is a significant synergistic effect between the DBD plasma and Ag/CeO_2 catalyst in HCHO oxidation process.

Regarding the large difference of $P(HCHO \rightarrow CO_2)$ in plasma-induced HCHO removal over Ag/CeO_2 and fused silica pellets (86% and 6%, at E_{in} = 108 J l^{-1}), one reasonable explanation is that these two kinds of filled pellets may have very different oxidation ability for CO under plasma conditions. In order to verify our hypothesis, some specially-designed CO oxidation experiments were carried out. Fig. 3 shows the CO oxidation percentages, $P(CO \rightarrow CO_2)$, obtained from a feed gas mixture (200 ppm CO, 21.0% O_2, 1.0% H_2O in N_2) passing through Ag/CeO_2 and fused silica pellets at 70 °C with and without discharges (E_{in} = 0). Without discharges, on the contrast to fused silica pellets, which are totally chemically inert to CO, Ag/CeO_2 catalyst can oxidize 32% of CO to CO_2. Under plasma conditions, with increasing E_{in}, $P(CO \rightarrow CO_2)$ over Ag/CeO_2 increases much faster than that over fused silica pellets. For example, at E_{in} = 108 $J \cdot l^{-1}$, $P(CO \rightarrow CO_2)$ values for Ag/CeO_2 and fused silica pellets are 80% and 5%, respectively.

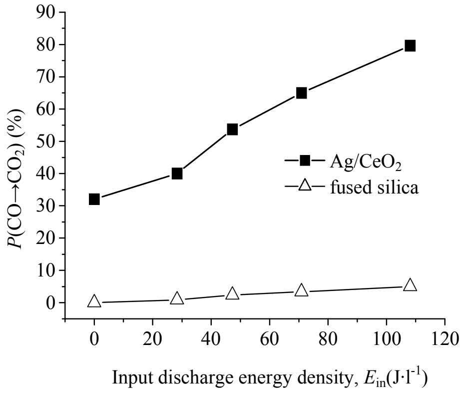

Fig. 3 CO oxidation percentage, $P(CO \rightarrow CO_2)$, over Ag/CeO_2, γ-Al_2O_3 and fused silica pellets with and without discharges (200 ppm CO, 21.0% O_2, 1.0% H_2O in N_2, E_{in} = 0 corresponds the condition without discharges).

From the data shown in Fig. 3, the values of $P(CO \rightarrow CO_2)$ from pure plasma-induced (discharges over fused silica pellets, E_{in}=108 $J \cdot l^{-1}$), pure catalytic (over Ag/CeO_2 without discharges) and plasma-catalytic oxidation (discharges over Ag/CeO_2, E_{in}=108 $J \cdot l^{-1}$) of CO are 5%, 32% and 80%, respectively. There is also a significant synergistic effect between the DBD plasma and Ag/CeO_2 catalyst in CO oxidation process.

This significant synergistic effect between the DBD plasma and Ag/CeO_2 catalyst in CO and HCHO oxidation process could be well explained by the two kinds of plasma-assisted catalytic redox circles. From literature, Ag_2O and CeO_2, though less active than Ag/CeO_2 composite, are also fine catalysts for CO oxidation at higher temperatures [10,11]. Regarding the mechanism of the CO plasma-catalytic oxidation over separated Ag_2O and CeO_2 catalysts, initially, Ag_2O or CeO_2 itself may convert to Ag or Ce_2O_3 and release one oxygen atom, which reacts with CO to produce CO_2. Without plasmas, at higher temperatures, the O_2 can re-oxidize Ag into Ag_2O (or Ce_2O_3 into CeO_2) and reinitiate the redox circle. However, under plasma conditions, plasma-generated O or HO_2 radicals are very likely able to re-oxidize Ag to Ag_2O or Ce_2O_3 to CeO_2 at room temperature. There also some conjugated redox circles between Ag-Ag_2O and Ce_2O_3-CeO_2 inter-conversions for CO catalytic oxidation via discharges over Ag/CeO_2 catalyst, the analog of which without plasmas was proposed by Lou et al. [10] in their $Ag/CeO_2/Al_2O_3$ catalytic system for CO oxidation at higher temperatures. In these conjugated redox circles, Ag_2O first reacts with CO in generating Ag and CO_2, then CeO_2 reacts with Ag to produce Ag_2O and Ce_2O_3. Finally, the plasma-generated O or HO_2 radicals re-oxidize Ce_2O_3 to CeO_2 and complete the whole redox circle. Compared with the two separated redox circles for Ag/Ag_2O and CeO_2/Ce_2O_3, these conjugated circles should have a higher total reaction rate for CO catalytic oxidation [10].

Similar plasma-assisted catalytic redox circles can be also used for the oxidation of HCHO and its oxidation intermediates (e.g. HCOOH).

In all the experiments reported in this work, it was found, that the total amount of NO, NO_2 and N_2O in the outflow gas, which could be produced from N_2 and O_2 in the plasmas, is smaller than 10 ppm. It was found that in the pellets-filled atmospheric pressure DBD plasmas, significant amount of NO_x (>50 ppm) can only be produced from N_2 and O_2 at higher temperatures (>300 °C) over some catalysts [12].

3.2 HCHO Specific Energy Consumption Per HCHO Molecule Converted

The influence of input discharge energy density, E_{in}, on HCHO specific energy consumption per HCHO molecule converted, ε, via using the plasma-catalytic reactor filled with Ag/CeO_2 pellets and the standard feed gas mixture (276 ppm HCHO, 21.0% O_2, 1.0% H_2O in N_2) with GHSV of 16500 h^{-1}

is shown in Fig. 4. Over the whole E_{in} range investigated, ε show monotonic increase with the rising E_{in}.

When increasing E_{in}, more active species, which can react with HCHO to remove HCHO, are generated by plasma, therefore, the probability of impact between every HCHO molecule with these active species increases, thus increasing the removal efficiency of formaldehyde. However, the probability of impact of every active species with HCHO molecules decreases when the amount of active species increases. Therefore, these active species can not be used effectively, thus resulting in ε increase.

With the Ag/CeO_2 pellets-filled DBD reactor, the dependence of HCHO specific energy consumption per HCHO moleculer converted, ε, and $P(HCHO\rightarrow CO_x)$ on HCHO initial concentration in the feed gas (21% O_2, 1.0% H_2O in N_2, GHSV = 16500 h^{-1}) at E_{in} = 108 J l^{-1} is shown in figure 5. With E_{in} = 108 J l^{-1}, ε decreased sharply from 92 eV/molecule to 47 eV/molecule as initial concentration was raised from 276 ppm to 635 ppm. Then, ε slowly decreased to 42 eV/molecule when initial concentration rose to 965 ppm.

The dramatic decrease of $P(HCHO\rightarrow CO_x)$ from 99% to 62.5% with the inlet HCHO concentrations rising from 276 to 965 ppm indicates that the amount of active species including the plasma-generated high-energy electrons, active radicals and excited species, is in the range comparable to the number of HCHO molecules to be removed.

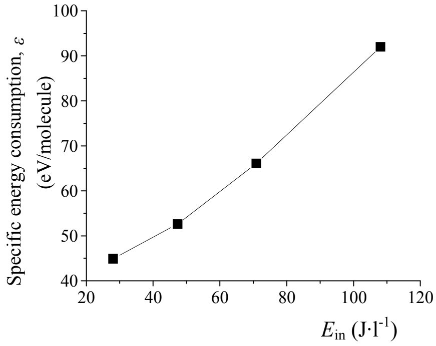

Fig. 4 The influence of input discharge energy density, E_{in}, on HCHO specific energy consumption per HCHO molecule converted. (276 ppm HCHO, 21% O_2, 1.0% H_2O in N_2)

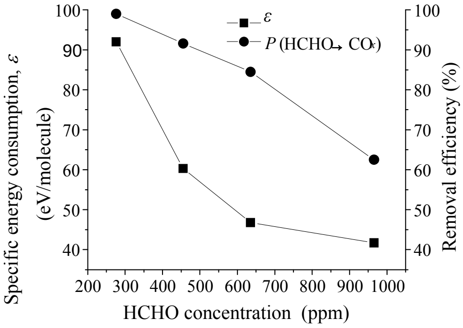

Fig 5 HCHO specific energy consumption per HCHO moleculer converted, ε, and $P(HCHO\rightarrow CO_x)$ as functions of its initial concentration. (21% O_2, 1.0% H_2O in N_2, GHSV = 16500 h^{-1})

When increasing the initial concentration of formaldehyde at E_{in} = 108 J·l^{-1}, the probability of impact of every active species with the HCHO molecules increases. These active species can be used effectively, thus resulting in ε decrease. For every formaldehyde molecule, the increase in the amounts of formaldehyde molecule means the decrease in the probability of impact between formaldehyde molecule and the active species , thus resulting in $P(HCHO\rightarrow CO_x)$ decrease.

4 CONCLUSIONS

- Plasma-catalytic oxidation of formaldehyde has been studied via dielectric barrier discharges over Ag/CeO_2 at atmospheric pressure and 70 ℃. With a feed gas mixture of 276 ppm HCHO, 21.0% O_2, 1.0% H_2O in N_2, -99% of formaldehyde can be effectively destructed with a 86% oxidative conversion into CO_2 at GHSV of 16500 h^{-1} and input discharge energy density of 108 J·l^{-1}. The profound synergistic effects between the DBD plasma and Ag/CeO_2 catalyst observed in HCHO and CO oxidation experiments can be well explained by the plasma-assisted catalytic redox circles including Ag-Ag_2O and Ce_2O_3-CeO_2 inter-conversions.
- The energy consumption of removal formaldehyde from gas streams via using the plasma-catalytic reactor filled with Ag/CeO_2 pellets has been studied in this work. HCHO specific energy consumption per HCHO molecule converted, ε, decreases by increasing HCHO initial concentration, and increases by increasing E_{in}. With a feed gas mixture of 276 ppm HCHO, 21.0% O_2, 1.0% H_2O in N_2, ε is only 92eV at GHSV of 16500 h^{-1} and E_{in} = 108 J·l^{-1}, when the reactor is filled with Ag/CeO_2 pellet. When HCHO initial concentration is increased to 965 ppm, HCHO removal efficiency, $P(HCHO\rightarrow CO_x)$, is decreased to 63%, HCHO specific energy consumption per HCHO molecule converted, ε, decreases to 42eV.

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